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*Published in:*  
Journal of Chemical Physics

*DOI:*  
[10.1063/1.454185](https://doi.org/10.1063/1.454185)

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*Document Version*  
Publisher's PDF, also known as Version of record

*Publication date:*  
1988

[Link to publication in University of Groningen/UMCG research database](#)

*Citation for published version (APA):*

de Lange, P. J., Drabe, K. E., & Kommandeur, J. (1988). Radiationless transitions and the quantum yield for nonresonant light scattering. *Journal of Chemical Physics*, 88(2), 588-597.  
<https://doi.org/10.1063/1.454185>

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Citation: [The Journal of Chemical Physics](#) **88**, 588 (1988); doi: 10.1063/1.454185

View online: <https://doi.org/10.1063/1.454185>

View Table of Contents: <http://aip.scitation.org/toc/jcp/88/2>

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# Radiationless transitions and the quantum yield for nonresonant light scattering

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(Received 20 July 1987; accepted 15 September 1987)

The quantum yield for fluorescence can be defined as the ratio of the amount of light scattered as fluorescence or as Rayleigh or Raman scattering to the amount of light removed from an incident beam. Clearly then the quantum yield should go to one for a nonresonant excitation. The conventional theory of radiationless transitions (the Bixon-Jortner model) does not yield this result. We therefore postulate an intermediate state in the radiationless pathway. Then the model does yield the desired frequency dependence of the quantum yield. It may be that the arbitrary variation of the quantum yields of organic molecules may be due to the absence or presence of such an intermediate state.

## INTRODUCTION

The theory of radiationless transitions<sup>1,2</sup> in molecules is by now well established. Such effects as quantum beats,<sup>3,4</sup> exponential,<sup>1</sup> and biexponential<sup>5</sup> decay can be readily explained. In a theoretical sense in the limit of linear response, there are very few questions that have remained unanswered.

In this paper we want to focus on the quantum yield. As is well known, interference of the "prepared" or "doorway" state  $|S\rangle$  with a background of (almost) continuous "dark" states  $\{|1\rangle\}$  leads to such a rapid distribution of the amplitude of the prepared state with the radiative property over the many background states that at times longer than  $(2\pi\langle v^2\rangle\rho)^{-1}$ , where  $\langle v^2\rangle$  is the rms interaction with and  $\rho$  the density of the background states, no, or hardly any light is emitted any more, and the quantum yield is given by  $\Gamma_r/(\Gamma_r + 2\pi\langle v^2\rangle\rho)$ .

The equations yielding this result are exact in the weak field limit, and since both fluorescence and nonresonant light scattering (NRLS) are linear processes they should hold for fluorescence as well as for NRLS. This was shown already some time ago by Mukamel and Jortner<sup>6</sup> in a theoretical paper, in which they explained the results of Rousseau and Williams<sup>7</sup> on the fluorescence of iodine and in which they obtained a so-called "fast" component by exciting a transition close to but not on resonance.

There is, however, a problem, which did not play a role in the iodine work since there they took the quantum yield to be one. In general, for larger molecules the quantum yield can be very low, and since NRLS comes from the same theory, the quantum yield might also be expected to be low for nonresonant excitation. Indeed, the conventional form in which the theory of radiationless transitions is cast, leads to this result. Nevertheless, Raman spectroscopists (Raman is one form of NRLS) look for nonfluorescent molecules, i.e.,

molecules with a very low quantum yield and then proceed to measure the Raman spectrum! The same appears to hold for people measuring Rayleigh scattering, they do not for a minute worry about the quantum yield of the molecules they are scattering off. And, in concurrence, conventional theoretical treatments of Raman and Rayleigh scattering do not even take the quantum yield into account!

In this paper we endeavor to resolve this apparent contradiction and it will become clear that there is a necessity for the postulate that in all molecules with a low quantum yield through interaction with a dense manifold, there must at least be one state in this manifold which interacts much more strongly with the doorway state than the others.

To set the stage for our discussion we will first define quantum yield properly, then show that the conventional theory of radiationless transitions does indeed lead to a low quantum yield for NRLS.

It will then also become clear what measures must be taken to let the properly defined quantum yield go to one for nonresonant excitation. We will finally endeavor to apply our theoretical result to further clarify our previous experimental results for NRLS in pyrazine.<sup>8</sup>

## THE QUANTUM YIELD

Usually the quantum yield is defined as the total number of photons emitted divided by the total number of photons absorbed. In this definition, the meaning of "photons absorbed" is somewhat ambiguous. Not only the photons which remain "inside" the molecule have to be taken into account, but also the photons which are scattered out of the beam. So with photons absorbed one means the total number of photons removed from the incident beam. To avoid confusion we will call this quantity the photon loss. The quantum yield, which is now given by the number of photons emitted divided by the photon loss, will be low if photons remain inside the molecule for longer times, but it should approach one for nonresonant light scattering.

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## THE PHOTON LOSS OF THE INCIDENT BEAM AND THE SHORT TIME EMISSION INTENSITY

Since we are interested in nonresonant excitation the number of photons removed from the incident beam will depend on the laser envelope function and its position in frequency space. We must therefore treat excitations by lasers which span a limited part of the frequency domain.

Consider the absorption of an induced dipole moment  $\hat{u}(t)$  in the electric field of the laser  $\hat{\chi}(t)$ . The total energy dissipated is given by<sup>9</sup>

$$P = \int_{-\infty}^{\infty} \hat{\chi}(t) d\hat{u}(t) = \int_{-\infty}^{\infty} \hat{\chi}(t) \frac{d\hat{u}(t)}{dt} dt. \quad (1)$$

If we assume linear response, the induced dipole moment can be written as the convolution of the electric field with  $\hat{A}_s(t)$ ,<sup>9</sup>

$$\hat{u}(t) = \hat{\chi}(t) * \hat{A}_s(t), \quad (2)$$

in which  $\hat{A}_s(t)$  is the response of the dipole on a  $\delta$  pulse in time. Both equations can be transformed to  $\omega$  space using Parseval's rule and the convolution theorem. Writing  $\chi(\omega)$ ,  $u(\omega)$ , and  $A_s(\omega)$  as the Fourier transform of, respectively,  $\hat{\chi}(t)$ ,  $\hat{u}(t)$ , and  $\hat{A}_s(t)$ , we get for Eq. (1),

$$P = \frac{1}{2\pi} \int_{-\infty}^{\infty} i\omega \chi(\omega) u(\omega) d\omega, \quad (3)$$

and for Eq. (2),

$$u(\omega) = \chi(\omega) A_s(\omega). \quad (4)$$

Substitution of Eq. (4) into Eq. (3) gives

$$P = \frac{1}{2\pi} \int_{-\infty}^{\infty} i\omega |\chi(\omega)|^2 A_s(\omega) d\omega, \quad (5)$$

and since  $P$  must be real,

$$P = \frac{1}{2\pi} \int_{-\infty}^{\infty} \omega |\chi(\omega)|^2 \cdot -\text{Im}[A_s(\omega)] d\omega. \quad (6)$$

If we want to have a measure of the number of photons which are removed from the beam we have to divide this energy by the energy per photon, so we get for the total photon loss  $S'$  of the incident beam

$$S' = C \int_{-\infty}^{\infty} |\chi(\omega)|^2 \cdot -\text{Im}[A_s(\omega)] d\omega. \quad (7)$$

The constant  $C$  takes into account the sensitivity of the detector, the spatial angle detected, etc. For convenience we put it equal to one. In the case that we consider one singlet state  $|s\rangle$ , carrying all the radiative transition probability and interacting with a dense background of dark states  $\{|l\rangle\}$ ,  $A_s(\omega)$  is given in the rotating wave approximation by Ref. (2),

$$A_s(\omega) = 1 / \left( \omega - \omega_s - \sum_l \frac{v_{sl}^2}{\omega - \omega_l} + i\Gamma_r/2 \right). \quad (8)$$

In this equation,  $\omega_s$  is the energy of the state  $|s\rangle$ ,  $\omega_l$  are the energies of  $\{|l\rangle\}$ ,  $\{v_{sl}\}$  are the matrix elements coupling  $|s\rangle$  and  $\{|l\rangle\}$ , and  $\Gamma_r$  is the radiative width of the state  $|s\rangle$ . Conventionally,  $\omega_s$  is taken to be zero, so we get

$$\begin{aligned} S' &= \int_{-\infty}^{\infty} |\chi(\omega)|^2 \\ &\times -\text{Im} \left[ 1 / \left( \omega - \sum_l \frac{v_{sl}^2}{\omega - \omega_l} + i\Gamma_r/2 \right) \right] d\omega \\ &= \frac{\Gamma_r}{2} \int_{-\infty}^{\infty} |\chi(\omega)|^2 \\ &\times \left\{ 1 / \left[ \left( \omega - \sum_l \frac{v_{sl}^2}{\omega - \omega_l} \right)^2 + \Gamma_r^2/4 \right] \right\} d\omega \\ &= \frac{\Gamma_r}{2} \int_{-\infty}^{\infty} |C_s(\omega)|^2 d\omega, \end{aligned} \quad (9)$$

where

$$\begin{aligned} C_s(\omega) &= \chi(\omega) A_s(\omega) \\ &= \chi(\omega) / \left( \omega - \sum_l \frac{v_{sl}^2}{\omega - \omega_l} + i\Gamma_r/2 \right), \end{aligned} \quad (10)$$

the part of the total amplitude  $A_s(\omega)$ , excited by the laser  $\chi(\omega)$ . Using a white laser [ $\chi(\omega) = 1$ ] we want  $S'$  to be normalized to one:

$$S = \frac{\Gamma_r}{2\pi} \int_{-\infty}^{\infty} |C_s(\omega)|^2 d\omega. \quad (11)$$

Fluorescence is spontaneous emission, which is due to the "amount" of singlet excited:  $|C_s(\omega)|^2$  (not  $|A_s(\omega)|^2$ ). Its time behavior is given by  $|\hat{C}_s(t)|^2$ , where  $\hat{C}_s(t)$  is the Fourier transform of  $C_s(\omega)$ :

$$E(t) = \Gamma_r |\hat{C}_s(t)|^2. \quad (12)$$

And the total emission is given by

$$E = \Gamma_r \int_{-\infty}^{\infty} |\hat{C}_s(t)|^2 dt \quad (13)$$

which becomes, using Parseval's theorem,

$$E = \frac{\Gamma_r}{2\pi} \int_{-\infty}^{\infty} |C_s(\omega)|^2 d\omega. \quad (14)$$

Note that the right-hand sides of Eqs. (14) and (11) are the same. Therefore, the ratio between  $S$  and  $E$  will always be 1 and so will the quantum yield for every laser envelope function  $\chi(\omega)$ . This is indeed so, if we could measure for infinite time, i.e., if the integration could be carried out to infinity.

As is well known, this is not the case. We have to take into account that the determination of a quantum yield is a mark of experimental limitation. After a fast "dephasing" of the states, there is still energy in the molecule, but it comes out as visible photons so slowly that any apparatus will fail to measure it. (We explicitly exclude emissions in other parts of the spectrum here.) Therefore, to find the experimental quantum yield we have to integrate time space only up to a finite time  $T$ , say  $T \approx 3 \times (2\pi \langle v^2 \rangle \rho)^{-1}$ , after which the experimenter sees no further light coming out. It is then possible to find a quantum yield lower than one.

Of course we can calculate the total photon loss  $S$  and the short time emission  $E^s$ , i.e., the emission intensity integrated over short times for different laser envelope functions using a computer, but given the need for a dense background and a proper sampling of all  $\omega$  space to obtain  $|C_s(\omega)|^2$ , this

procedure may quickly lead to erroneous results, particularly for nonresonant excitation. For two simple laser envelope functions we therefore developed approximations for the photon loss  $S$  and the short time emission  $E^s$  in an analytical manner and compare these results with our computer calculations.

(i) First we consider very broad band excitation, i.e., a  $\delta$  pulse in time and take for simplicity  $\chi(\omega) = 1$ . Then we have for Eq. (11),

$$S = \frac{\Gamma_r}{2\pi} \int_{-\infty}^{\infty} |C_s(\omega)|^2 d\omega = \frac{\Gamma_r}{2\pi} \cdot \frac{2\pi}{\Gamma_r} = 1. \quad (15)$$

For the short time emission  $E^s$  we get

$$E^s = \Gamma_r \int_{-\infty}^T \left| FT \left\{ 1 / \left( \omega - \sum_l \frac{v_{sl}^2}{\omega - \omega_l} + i\Gamma_r/2 \right) \right\} \right|^2 dt. \quad (16)$$

Usually now, the sum is replaced by an integral, because the levels  $\{|l\rangle\}$  are so closely spaced that their separations do not play any role on the time scale, which is significant for the emission. After replacing  $v_{sl}^2$  by its average  $\langle v^2 \rangle$  one finds by complex integration

$$- \sum_l \frac{v_{sl}^2}{\omega - \omega_l} \rightarrow i\pi \langle v^2 \rangle \rho = i\Gamma_{nr}/2. \quad (17)$$

We then have

$$\begin{aligned} E^s &= \Gamma_r \int_{-\infty}^T \left| FT \left\{ \frac{1}{\omega + i(\Gamma_{nr} + \Gamma_r)/2} \right\} \right|^2 dt \\ &= \Gamma_r \int_0^T \left| \exp \left[ - \frac{(\Gamma_{nr} + \Gamma_r)}{2} t \right] \right|^2 dt \\ &= \Gamma_r \int_0^T \exp[ - (\Gamma_{nr} + \Gamma_r) t ] dt \\ &\approx \Gamma_r / (\Gamma_{nr} + \Gamma_r). \end{aligned} \quad (18)$$

The experimental quantum yield is then given by  $Q = E^s/S = \Gamma_r / (\Gamma_{nr} + \Gamma_r)$ . This is a well-known result,

$$S \approx C \int_{W/2}^{W/2} \frac{\sin^2(\pi\rho\omega) d(\pi\rho\omega)}{(k_1^2 + k_2^2) \sin^2(\pi\rho\omega) + 2k_1 \cos(\pi\rho\omega) \sin(\pi\rho\omega) + \cos^2(\pi\rho\omega)} \quad (24)$$

with

$$C = 2\Gamma_r / (\pi^2 \Gamma_{nr}^2 \rho),$$

$$k_1 = -2\Delta/\Gamma_{nr} \text{ and } k_2 = \Gamma_r/\Gamma_{nr}.$$

The integration can be performed analytically and one can show that in the limit for large detuning ( $\Delta \gg \Gamma_{nr}, \Gamma_r$ ) we get (Appendix A)

$$S \approx \frac{W}{2\pi\Delta^2} (\Gamma_{nr} + \Gamma_r). \quad (25)$$

the statistical limit (1). Note that this result is obtained only if we do not make use of Eq. (17) in calculating the photon loss (otherwise one obtains a quantum yield of one). Physically, Eq. (17) means that we throw away all long time emission, and therefore we can never calculate the correct photon loss of the incident beam, we would not include the photons that remain inside the molecule.

(ii) As a second illustration we now consider a nonresonant laser, which has in  $\omega$  space a block shape of width  $W$ . Then we obtain from Eq. (11) for the photon loss:

$$S = \frac{\Gamma_r}{2\pi} \int_{\Delta - W/2}^{\Delta + W/2} \left| 1 / \left( \omega - \sum_l \frac{v_{sl}^2}{\omega - \omega_l} + i\Gamma_r/2 \right) \right|^2 d\omega, \quad (19)$$

where  $\Delta$  is the detuning of the laser and  $W$  is the width of the laser. In calculating the photon loss we are not allowed to replace the sum by an integral. Instead, we have to evaluate the discrete sum. This can easily be done if we take the levels  $|l\rangle$  equally spaced and if we take  $v_{sl}^2 = \langle v^2 \rangle$ .

We obtain

$$\sum_l \frac{v_{sl}^2}{\omega - \omega_l} = \pi \langle v^2 \rangle \rho \cot(\pi\rho\omega) = \frac{\Gamma_{nr}}{2} \cot(\pi\rho\omega). \quad (20)$$

Equation (19) then becomes

$$S = \frac{\Gamma_r}{2\pi} \int_{\Delta - W/2}^{\Delta + W/2} \left| \frac{1}{\omega - \frac{1}{2} \Gamma_{nr} \cot(\pi\rho\omega) + i\Gamma_r/2} \right|^2 d\omega. \quad (21)$$

Because of the periodicity of  $\cot(\pi\rho\omega)$  we may also write

$$\begin{aligned} S &= \frac{\Gamma_r}{2\pi} \\ &\times \int_{-W/2}^{W/2} \left| \frac{1}{\Delta + \omega - \frac{1}{2} \Gamma_{nr} \cot(\pi\rho\omega) + i\Gamma_r/2} \right|^2 d\omega. \end{aligned} \quad (22)$$

In the limit where the detuning of the laser is much larger than its width ( $\Delta \gg W$ ) we have

$$S \approx \frac{\Gamma_r}{2\pi} \int_{-W/2}^{W/2} \left| \frac{1}{\Delta - \frac{1}{2} \Gamma_{nr} \cot(\pi\rho\omega) + i\Gamma_r/2} \right|^2 d\omega. \quad (23)$$

This can, after rearrangement, be rewritten to

For the short time emission we may replace the sum of Eq. (17) by an integral and we get from Eq. (13):

$$E^s = \Gamma_r \int_{-\infty}^T \left| FT \left\{ \frac{\chi(\omega)}{\omega + i(\Gamma_{nr} + \Gamma_r)/2} \right\} \right|^2 dt. \quad (26)$$

Because of the fact that by this replacement all long-time emission is really thrown away [compare Eq. (18)], we may also write

$$E^s = \Gamma_r \int_{-\infty}^{\infty} \left| FT \left\{ \frac{\chi(\omega)}{\omega + i(\Gamma_{nr} + \Gamma_r)/2} \right\} \right|^2 dt \quad (27)$$

which equals (Parseval)

$$\begin{aligned} E^s &= \frac{\Gamma_r}{2\pi} \int_{-\infty}^{\infty} \left| \frac{\chi(\omega)}{\omega + i(\Gamma_{nr} + \Gamma_r)/2} \right|^2 d\omega \\ &= \frac{\Gamma_r}{2\pi} \int_{-W/2}^{W/2} \left| \frac{1}{\Delta + \omega + i(\Gamma_{nr} + \Gamma_r)/2} \right|^2 d\omega. \end{aligned} \quad (28)$$

In the limit of large detuning ( $\Delta \gg W, \Gamma_{nr}, \Gamma_r$ ), we can approximate this by

$$E^s \approx \frac{\Gamma_r}{2\pi} \frac{W}{\Delta^2}. \quad (29)$$

And the experimental quantum yield can be calculated:

$$Q = \frac{E^s}{S} = \frac{\Gamma_r}{\Gamma_{nr} + \Gamma_r}. \quad (30)$$

In Table I we compare these approximate analytical results with computer results and we obtain satisfactory agreement. The same results for the quantum yield were also obtained by computer calculations using a Gaussian laser envelope function. The conclusion is strangely enough that the quantum yield remains low for nonresonant excitation. In terms of Eq. (26) this is due to the fact that since  $\Gamma_{nr}$  is not a function of  $\omega$ , it will lead to a coupling to the background at all detunings! Such a result was also arrived at by Mukamel and Shan.<sup>10</sup> As long as there is a background manifold the quantum yield is low. It only rises to one, when the excitation is in a range, where the manifold does not continue anymore. In

the next section we will see what we can do to obtain a proper behavior of the quantum yield even when the background is present at all frequencies.

## THE INTERMEDIATE STATE

The interaction of an  $S_1$  state with an  $S_0$  manifold will seldom be homogeneous. The vibrational states making up  $\{S_0\}$  at the energy of  $S_1$  consist of all permutations of the vibrational quantum numbers of the molecular modes. Some of these will have preponderance of a  $v = 1$  state of a particular mode, and if  $S_1$  is a vibrationless state (all  $v' = 0$ ), and if the mode is, for instance, Herzberg-Teller active, that state can be much more strongly coupled than others consisting of combinations of higher quantum numbers.

It seems reasonable then for our quantum yield problem to postulate (at least) one "intermediate" state, which has a much stronger interaction. In its turn this state is coupled to the other background states. Of course there can (and there will be) more such strongly coupled states, but for the sake of argument one will do. By reasoning very similar to the one used to obtain Eq. (10), we then have for  $C_s(\omega)$ :

$$C_s(\omega) = \chi(\omega) / \left\{ \omega - \left[ v_{sl}^2 / \left( \omega - \omega_l - \sum_k \frac{v_{lk}^2}{\omega - \omega_k} \right) \right] + i\Gamma_r/2 \right\}, \quad (31)$$

where  $\omega_l$  is the strongly coupled state and  $\{\omega_k\}$  are the manifold of weakly coupled background states.

If we want to calculate the short time emission we again are not interested in the small  $\Delta\omega$ , and therefore, long time fluctuations in the background, and therefore, we are allowed to replace the sum  $\sum_k v_{lk}^2 / (\omega - \omega_k)$  by  $i\Gamma_l/2$ ,

TABLE I. Comparison of analytical and numerical results.

(i) Resonant			
$\chi(\omega) = 1$		$\Gamma_{nr}/\Gamma_r = 99$	$N_F^a = 131\,072$
	Analytical expression	Analytical value	Numerical value
$S$	1	1.000	0.972
$E^s$	$\Gamma_r(\Gamma_r + \Gamma_{nr})^{-1}$	0.010	0.011
$Q$	$\Gamma_r(\Gamma_r + \Gamma_{nr})^{-1}$	0.010	0.011
(ii) Nonresonant			
$\chi(\omega) = 1$		$(\Delta - W/2) < \omega < (\Delta + W/2)$	
$\chi(\omega) = 0$		$\omega < (\Delta - W/2) \wedge \omega > (\Delta + W/2)$	
$\Gamma_{nr}/\Gamma_r = 99$		$W/\Gamma_r = 100$	$\Delta/\Gamma_r = 500 \quad N_F = 131\,072$
	Analytical expression	Analytical value	Numerical value
$S$	$\frac{W}{2\pi\Delta^2}(\Gamma_{nr} + \Gamma_r)$	$0.637 \times 10^{-2}$	$0.711 \times 10^{-2}$
$E_s$	$\frac{W}{2\pi\Delta^2}(\Gamma_r)$	$0.637 \times 10^{-4}$	$0.776 \times 10^{-4}$
$Q$	$\Gamma_r(\Gamma_r + \Gamma_{nr})^{-1}$	0.010	0.011

<sup>a</sup>  $N_F$  = number of points in  $\omega$  space used in Fourier transformation.

$$E^s = \Gamma_r \int_{-\infty}^T \left| FT \left\{ \chi(\omega) / \left( \omega - \frac{v_{sl}^2}{\omega - \omega_l + i\Gamma_l/2} + i\Gamma_r/2 \right) \right\} \right|^2 dt \quad (32)$$

$$= \Gamma_r \int_{-\infty}^T \left| FT \left\{ \chi(\omega) / \left[ \omega - \frac{v_{sl}^2(\omega - \omega_l)}{(\omega - \omega_l)^2 + \Gamma_l^2/4} + i \frac{v_{sl}^2 \Gamma_l/2}{(\omega - \omega_l)^2 + i\Gamma_l^2/4} + i\Gamma_r/2 \right] \right\} \right|^2 dt \quad (33)$$

with  $\Gamma_l = 2\pi \langle v_{lk}^2 \rangle \rho_k$ .

If we compare this equation with Eq. (26) we have a new  $\Gamma_{nr}$ ,

$$\Gamma_{nr}^* = \frac{v_{sl}^2 \Gamma_l}{(\omega - \omega_l)^2 + \Gamma_l^2/4}$$

which now depends on  $\omega$ . This means that the quantum yield becomes a function of the detuning from  $\omega_l$  or, if we chose  $\omega_l$  not too far from  $\omega_s$ , of the detuning from  $\omega_s$ . Let us approximate the quantum yield in a simple case,  $\omega_l = \omega_s = 0$ , using the same laser envelope functions as in the previous section.

(i) The resonant case [ $\chi(\omega) = 1$ ]. The total photon loss is given by

$$\begin{aligned} S &= \frac{\Gamma_r}{2\pi} \int_{-\infty}^{\infty} |C_s(\omega)|^2 d\omega \\ &= \frac{\Gamma_r}{2\pi} \int_{-\infty}^{\infty} \left| 1 / \left[ \omega - \frac{v_{sl}^2}{\omega - \Sigma_k v_{lk}^2 / (\omega - \omega_k)} + i\Gamma_r/2 \right] \right|^2 d\omega \\ &= \frac{\Gamma_r}{2\pi} \cdot \frac{2\pi}{\Gamma_r} = 1, \end{aligned} \quad (34)$$

because the state  $|S\rangle$  remains normalized.

The short time emission is given by Eq. (32), which can be written as (we have thrown away the long time emission)

$$E^s = \frac{\Gamma_r}{2\pi} \int_{-\infty}^{\infty} \left| 1 / \left( \omega - \frac{v_{sl}^2}{\omega + i\Gamma_l/2} + i\Gamma_r/2 \right) \right|^2 d\omega,$$

where we have used Parseval's theorem.

This can be rearranged:

$$\begin{aligned} E^s &= \frac{\Gamma_r}{2\pi} \left( \int_{-\infty}^{\infty} \frac{\omega^2}{\omega^4 + b\omega^2 + a} d\omega \right. \\ &\quad \left. + \int_{-\infty}^{\infty} \frac{\Gamma_l^2/4}{\omega^4 + b\omega^2 + a} d\omega \right) \end{aligned} \quad (36)$$

with

$$a = \left( v_{sl}^2 + \frac{\Gamma_r \Gamma_l}{4} \right)^2 \quad (35)$$

and

$$b = \frac{1}{4} \Gamma_r^2 + \frac{1}{4} \Gamma_l^2 - 2v_{sl}^2.$$

The integrals can be evaluated and in the case of  $(\Gamma_r \ll 2v_{sl} < \Gamma_l)$ ,  $(\Gamma_r \Gamma_l \ll 4v_{sl}^2)$  we can approximate  $E_s$  by

$$E_s \approx \frac{\Gamma_r}{2\pi} \cdot \frac{\pi \Gamma_l}{2v_{sl}^2} = \frac{\Gamma_r \Gamma_l}{4v_{sl}^2}. \quad (37)$$

For details see Appendix B.

Therefore the quantum yield is given by

$$Q = \frac{E_s}{S} = \frac{\Gamma_r \Gamma_l}{4v_{sl}^2}. \quad (38)$$

This result can be obtained much faster by taking the value of  $\Gamma_{nr}^*$  near resonance and substitute this into the equation

$$Q = \frac{\Gamma_r}{\Gamma_r + \Gamma_{nr}^*} = \frac{\Gamma_r}{\Gamma_r + (4v_{sl}^2/\Gamma_l)}. \quad (39)$$

For  $\Gamma_r \ll 4v_{sl}^2/\Gamma_l$ , Eq. (39) reduces to Eq. (38), but we prefer Eq. (39) because it is more general.

(ii) The nonresonant case

$$\chi(\omega) = 1 \quad \text{for } (\Delta - W/2) < \omega < (\Delta + W/2),$$

$$\chi(\omega) = 0 \quad \text{for } \omega < (\Delta - W/2) \text{ and for } \omega > (\Delta + W/2).$$

For the total photon loss we obtain from Eq. (34):

$$\begin{aligned} S &= \frac{\Gamma_r}{2\pi} \int_{-W/2}^{W/2} \left| 1 / \left[ \Delta + \omega - \frac{v_{sl}^2}{\Delta + \omega + \frac{1}{2} \Gamma_l \cot(\pi \rho \omega)} + i\Gamma_r/2 \right] \right|^2 d\omega \end{aligned} \quad (40)$$

and with  $\Delta \gg W/2$ ,

$$\begin{aligned} S &\approx \frac{\Gamma_r}{2\pi} \int_{-W/2}^{W/2} \left| 1 / \left[ \Delta - \frac{v_{sl}^2}{\Delta + \frac{1}{2} \Gamma_l \cot(\pi \rho \omega)} + \Gamma_r^2/4 \right] \right|^2 d\omega. \end{aligned} \quad (41)$$

In the limit of large  $\Delta$  this can be approximated by

$$S \approx \frac{\Gamma_r}{2\pi} \cdot \frac{W}{\Delta^2}. \quad (42)$$

For the short time emission we get after throwing away the long time emission and after using Parseval,

$$\begin{aligned} E_s &= \frac{\Gamma_r}{2\pi} \int_{-W/2}^{W/2} \left| 1 / \left( \Delta + \omega - \frac{v_{sl}^2}{\Delta + \omega + i\Gamma_l/2} + i\Gamma_r/2 \right) \right|^2 d\omega \end{aligned} \quad (43)$$

and with

$$\Delta \gg W/2$$

$$\approx \frac{\Gamma_r}{2\pi} \frac{W(\Delta^2 + \Gamma_l^2/4)}{(\Delta^2 - v_{sl}^2 - \Gamma_r \Gamma_l/4)^2 + \Delta^2 \frac{1}{4} (\Gamma_r + \Gamma_l)^2} \quad (44)$$

which can be approximated in the limit of large  $\Delta$  by

$$E_s \approx \frac{\Gamma_r}{2\pi} \frac{W\Delta^2}{\Delta^4} \approx \frac{\Gamma_r}{2\pi} \frac{W}{\Delta^2}. \quad (45)$$

Therefore, now the quantum yield ( $= E_s/S$ ) goes to one for large detuning. This result follows also from the fact that  $\Gamma_{nr}^*$  goes to zero for  $\omega \gg \omega_l$ , therefore  $Q = \Gamma_r/(\Gamma_r + \Gamma_{nr}^*)$  goes to one.

What happens if the intermediate state is not resonant

with the doorway state ( $\omega_l \neq 0$ )? In our first case,  $\chi(\omega) = 1$  for all  $\omega$ , the photon loss  $S$  is of course still one, but it appears to be fairly hopeless to find an analytical approximation for the short time emission  $E_S$ . We can, however, use the value of  $\Gamma_{nr}^*$  near resonance to approximate the quantum yield. We have

$$Q = \frac{\Gamma_r}{(\Gamma_r + \Gamma_{nr}^*)} = \Gamma_r / \left( \Gamma_r + \frac{v_{sl}^2 \Gamma_l}{\omega_l^2 + \Gamma_l^2/4} \right). \quad (46)$$

It is clear that the quantum yield at resonance depends on  $\omega_l$ , the position of the intermediate state. For a detuned laser the quantum yield goes to one, independent of  $\omega_l$ . All these analytical results were checked by computer calculations using the unapproximated formulas for

$$E_S = \Gamma_r \int_{-\infty}^{\infty} |\hat{C}_S(t)|^2 dt$$

and

$$S = \frac{\Gamma_r}{2\pi} \int_{-\infty}^{\infty} |C_S(\omega)|^2 d\omega.$$

A comparison for  $\omega_l = 0$  is given in Table II and for  $\omega_l/\Gamma_r = -200$  in Table III. Of course with a computer we can also calculate the quantum yield dependence on detuning for these values of  $\omega_l$ . The results using a Gaussian laser pulse are given in Figs. 1(a) and 1(b). Especially for  $\omega_l/\Gamma_r = 200$  there is a substantial amount of "noise" on the curve. This is caused by the discrete sampling of the  $\omega$  space and it was impossible to improve the results with our computer facilities. But the shape of the curve appears clear. The value of the photon loss  $S$ , as well as the value of  $\Gamma_{nr}^*/\Gamma_r$ , are given in the same figures. We conclude that by postulating

an intermediate state we can obtain the correct behavior of the quantum yield as a function of detuning.

We finally wish to point out that in this model the quantum yield as a function of detuning always will become 1 for large detuning, provided, of course, that the excitation bandwidth is finite. To this end we return to the basic equation (31). It is easily seen that for large detuning (i.e., large  $\omega$ ) there is only one pole of relevance, ( $\omega = -\Gamma_r/2$ ) both in calculating the photon loss as well as the short time emission. Crucial in this reasoning is the finite bandwidth of  $\chi(\omega)$ , which for large detuning wipes out all behavior for small  $\omega$ . It then follows immediately that the quantum yield for large detuning will approach one, irrespective of the various approximations made below Eq. (31).

## MANY INTERMEDIATE STATES

In general, in a complicated molecule there will be more than one vibrational state of  $S_0$  or  $T$  which can be active as an intermediate state. Some attention should therefore be paid to the case of one "light" state interacting with a discreet manifold  $\{|I\rangle\}$ , which in its turn is coupled to a dense manifold  $\{|k\rangle\}$ . We then have for  $A_s(\omega)$ :

$$A_s(\omega) = 1 / \left[ \omega - \sum_I \frac{v_{sl}^2}{\omega - \omega_l - \sum_k v_{lk}^2 / (\omega - \omega_k)} + i\Gamma_r/2 \right].$$

However, there are some subtle changes compared to the case of only one state. The states of manifold  $\{|I\rangle\}$  now obtain widths  $\Gamma_l$  due to the interaction with the background. For the  $\{|I\rangle\}$  manifold to remain discrete these widths

TABLE II. Comparison of analytical and numerical results.

(i) Resonant			
$\chi(\omega) = 1$ $\Gamma_l/\Gamma_r = 99$ $\omega_l = 0$ $v_{sl}^2/\Gamma_r = 225$ $N_F^* = 131\ 072$			
	Analytical expression	Analytical value	Numerical value
$S$	1	1.000	1.018
$E^S$	$\Gamma_r \left( \Gamma_r + \frac{4v_{sl}^2}{\Gamma_l} \right)^{-1}$	0.099	0.110
$Q$	$\Gamma_r \left( \Gamma_r + \frac{4v_{sl}^2}{\Gamma_l} \right)^{-1}$	0.099	0.108
(ii) Nonresonant			
$\chi(\omega) = 1$ $\omega < (\Delta - W/2) < \omega < (\Delta + W/2)$			
$\chi(\omega) = 0$ $\omega < (\Delta - W/2) \wedge \omega > (\Delta + W/2)$			
$\Gamma_l/\Gamma_r = 99$ $\omega_l = 0$ $v_{sl}^2/\Gamma_r = 225$ $W/\Gamma_r = 100$ $\Delta/\Gamma_r = 500$ $N_F = 131\ 072$			
	Analytical expression	Analytical value	Numerical value
$S$	$\frac{W}{2\pi\Delta^2}(\Gamma_r)$	$0.637 \times 10^{-4}$	$0.644 \times 10^{-4}$
$E^S$	$\frac{W}{2\pi\Delta^2}(\Gamma_r)$	$0.637 \times 10^{-4}$	$0.642 \times 10^{-4}$
$Q$	1	1.000	0.997

\* For  $N_F$  see Table I.

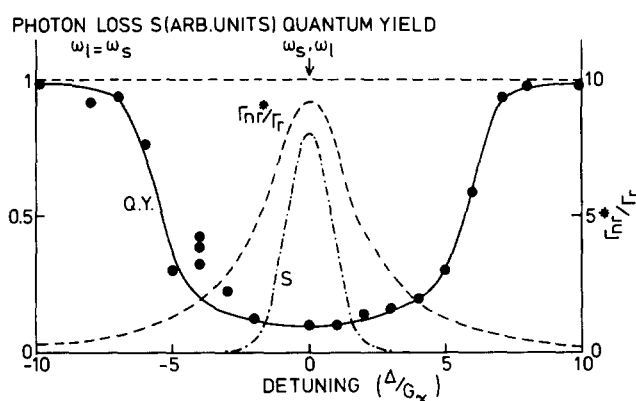


TABLE III. Comparison of analytical and numerical results.

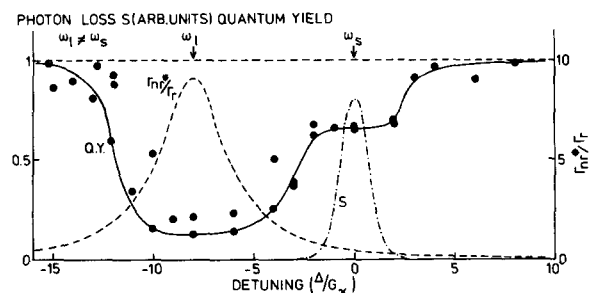
(i) Resonant			
$\chi(\omega) = 1$ $\Gamma_i/\Gamma_r = 99$ $\omega_i = -200/\Gamma_r$ $v_{si}^2/\Gamma_r = 225$ $N_F^* = 131072$			
	Analytical expression	Analytical value	Numerical value
$S$	1	1.000	0.988
$E^S$	$\Gamma_r \left( \Gamma_r + \frac{v_{si}^2 \Gamma_i}{\omega_i^2 + \Gamma_i^2/4} \right)^{-1}$	0.656	0.649
$Q$	$\Gamma_r \left( \Gamma_r + \frac{v_{si}^2 \Gamma_i}{\omega_i^2 + \Gamma_i^2/4} \right)^{-1}$	0.656	0.657

(ii) Nonresonant			
$\chi(\omega) = 1$ $(\Delta - W/2) < \omega < (\Delta + W/2)$			
$\chi(\omega) = 0$ $\omega < (\Delta - W/2) \wedge \omega > (\Delta + W/2)$			
$\Gamma_i/\Gamma_r = 99$ $\omega_i = -200/\Gamma_r$ $v_{si}^2/\Gamma_r = 225$ $W/\Gamma_r = 100$ $\Delta/\Gamma_r = 500$			
	Analytical expression	Analytical value	Numerical value
$Q$	1	1.000	0.989

\* For  $N_F$  see Table I.

(a)



(b)

FIG. 1. (a) The photon loss  $S$ , the quantum yield and  $\Gamma_{nr}^*/\Gamma_r$  as a function of the detuning of a Gaussian laser pulse from the doorway state. The intermediate state is resonant with the doorway state ( $\omega_i = 0$ ) and the width of the laser pulse is  $G_x$ . (b) Same as (a), but now for an intermediate state which is not resonant with the doorway state ( $\omega_i/\Gamma_r = -200$ ).

should be smaller than the separations in  $\{|I\rangle\}$ . Replacing  $\Sigma_k v_{ik}^2/(\omega - \omega_k)$  by  $i\Gamma_i/2$  and rearranging leads to

$$A_s(\omega) = 1 / \left\{ \omega - \sum_i \frac{v_{si}^2(\omega - \omega_i)}{(\omega - \omega_i)^2 + \Gamma_i^2/4} + i \left[ \sum_i \frac{v_{si}^2 \Gamma_i/2}{(\omega - \omega_i)^2 + \Gamma_i^2/4} + \Gamma_r/2 \right] \right\}.$$

As before, we can take

$$\Gamma_{nr}^* = \sum_i \frac{v_{si}^2 \Gamma_i}{(\omega - \omega_i)^2 + \Gamma_i^2/4}$$

and again this  $\Gamma_{nr}^*$  has become a function of  $\omega$ , but now peaking at every  $\omega_i$ . Therefore, the quantum yield will show dips at the various  $\omega_i$ . The resonant quantum yield, i.e., the quantum yield, where the absorption is strong will not be much affected by  $\omega_i$ 's not close to  $\omega_s$ , in that sense there is no qualitative and hardly a quantitative difference between the cases of one or more intermediate states. The difference does show up in the quantum yield for NRLS which should show variations along the manifold, being low, whenever the detuning reaches an intermediate state.

## CONCLUSION

It was shown in this paper that the conventional scheme for radiationless transitions does not offer an explanation for the experimental observation that the quantum yield goes to one for nonresonant excitation.

A way out of this problem is the postulation of one or more discrete intermediate states in the interaction between

the light state and the dense background states. Since the arguments here appear to be quite general, one might also invert them: a low quantum yield is a clear indication of a highly interacting intermediate state (almost) at resonance with the light state. This might explain the tremendous and seemingly arbitrary variations in quantum yields for organic molecules. Quite by accident such a state, which can be of triplet or singlet character, may or may not occur close to the singlet excited state.

Is there any way to check these notions experimentally? There might be. If a quantum yield is low, an intermediate state must be close. If it is, mixing with the singlet will lead to two states with a considerable singlet amplitude. The quantum yield will show a "dip" as a function of frequency at the positions of both these states. Typical interaction elements appear to be some 200 MHz or so.<sup>11-13</sup> The two dips should therefore be about that far apart and with present day lasers this should be accessible, if a proper determination of photon loss and emission can be attained. Obviously, if there are more intermediate states and if quantum yields for NRLS can be measured one might look for the many dips in the quantum yield as predicted by our scheme.

A somewhat different experiment may already have been reported. Some years ago, Jonkman, Drabe, and Kommandeur<sup>8</sup> reported nonresonant light scattering of pyrazine in a supersonic jet. It was found that the nonresonant light scattering *between* the rotational absorptions had an intensity of the same order of magnitude as the scattering (fluorescence at short times) *at* the rotational absorption. That is somewhat unexpected, since at first hand one would expect the scattered intensity to be much lower at nonresonance. The fact that it is *not*, is a strong indication that indeed the quantum yield for nonresonant is much higher than for resonant excitation.

## ACKNOWLEDGMENTS

The authors are much indebted to Professor S. Mukamel for suggesting the intermediate state. Part of the research has been supported by the Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for Pure Research (Z.W.O.).

## APPENDIX A

The total photon loss is given by

$$S \approx C \int_{-W/2}^{W/2} \frac{\sin^2(\pi\rho\omega)}{(k_1^2 + k_2^2)\sin^2(\pi\rho\omega) + 2k_1 \cos(\pi\rho\omega)\sin(\pi\rho\omega) + \cos^2(\pi\rho\omega)} d(\pi\rho\omega) \quad (\text{A1})$$

with  $C = 2\Gamma_r/(\pi^2\Gamma_{nr}^2\rho)$ ,  $k_1 = -2\Delta/\Gamma_{nr}$ , and  $k_2 = \Gamma_r/\Gamma_{nr}$ .

The integral can be evaluated,<sup>14</sup> and yields

$$S \approx C \frac{1}{4k_1^2 + (1 - k_1^2 - k_2^2)^2} \left\{ (k_1^2 + k_2^2 - 1)\pi\rho W \right. \\ \left. - k_1 \ln [\cos^2(\pi\rho W) + 2k_1 \sin(\pi\rho W)\cos(\pi\rho W) + (k_1^2 + k_2^2)\sin^2(\pi\rho W)] \right. \\ \left. + \frac{k_1^2 - k_2^2 + 1}{k_2} \arctan \left[ \frac{(k_1^2 + k_2^2)\tan(\pi\rho W) + k_1}{k_2} \right] \right\}_{-W/2}^{W/2} \quad (\text{A2})$$

$$\approx C \frac{1}{4k_1^2 + (1 - k_1^2 - k_2^2)^2} \left\{ (k_1^2 + k_2^2 - 1)\pi\rho W \right. \\ \left. - k_1 \ln \left[ \frac{\cos^2(\pi\rho \frac{1}{2} W) + k_1 \sin(\pi\rho W) + (k_1^2 + k_2^2)\sin^2(\pi\rho \frac{1}{2} W)}{\cos^2(\pi\rho \frac{1}{2} W) - k_1 \sin(\pi\rho W) + (k_1^2 + k_2^2)\sin^2(\pi\rho \frac{1}{2} W)} \right] \right. \\ \left. + \frac{k_1^2 - k_2^2 + 1}{k_2} \left( \arctan \left[ \frac{(k_1^2 + k_2^2)\tan(\pi\rho \frac{1}{2} W) + k_1}{k_2} \right] - \arctan \left[ \frac{(k_1^2 + k_2^2)\tan(-\pi\rho \frac{1}{2} W) + k_1}{k_1} \right] \right) \right\}. \quad (\text{A3})$$

Because the value of  $\arctan [f(\tan x)]$  lies between  $x - \pi$  and  $x + \pi$  and because  $x$  in our case  $(\pi\rho \frac{1}{2} W)$  is much larger than  $\pi$  we can well approximate the last part of Eq. (A3) by  $(k_1^2 - k_2^2 + 1)/k_2 \cdot \pi\rho W$ . {In this formula, the arctan does not represent the principle value. In  $\arctan [f(\tan x)]$  one must use that branch of the inverse tangent function upon which  $f(x)$  lies for any particular choice of  $x$ .}

Furthermore, if the density of background states  $\rho$  is high enough, the total photon loss cannot depend much on the exact width of the laser, so we may take  $\rho W$  close to an

integer. This makes the second part of Eq. (A3) almost zero. Then we have

$$S \approx C \frac{1}{4k_1^2 + (1 - k_1^2 - k_2^2)^2} \left[ (k_1^2 + k_2^2 - 1)\pi\rho W + \left( \frac{k_1^2 - k_2^2 + 1}{k_2} \right) \cdot \pi\rho W \right].$$

In the limit of large detuning ( $|k_1| \gg |k_2|, 1$ ) we get

$$\begin{aligned}
S &\approx \frac{2\Gamma_r}{\pi^2 \Gamma_{nr}^2 \rho} \cdot \frac{1}{k_1^4} \left( k_1^2 \pi \rho W + \frac{k_1^2}{k_2} \pi \rho W \right) \\
&\approx \frac{2\Gamma_r}{\pi \Gamma_{nr}^2} \left( \frac{W \Gamma_{nr}^2}{4\Delta^2} + \frac{W \Gamma_{nr}^2}{4\Delta^2} \cdot \frac{\Gamma_{nr}}{\Gamma_r} \right) \\
&\approx \frac{W \Gamma_r}{2\pi \Delta^2} \left( 1 + \frac{\Gamma_{nr}}{\Gamma_r} \right) \approx \frac{W}{2\pi \Delta^2} (\Gamma_r + \Gamma_{nr}).
\end{aligned}$$

## APPENDIX B

The short time emission is given by

$$\begin{aligned}
E^s &= \frac{\Gamma_r}{2\pi} \left( \int_{-\infty}^{\infty} \frac{\omega^2}{\omega^4 + b\omega^2 + a} d\omega \right. \\
&\quad \left. + \int_{-\infty}^{\infty} \frac{\Gamma_l^2/4}{\omega^4 + b\omega^2 + a} d\omega \right) \quad (B1)
\end{aligned}$$

with

$$a = \left( v_{sl}^2 + \frac{\Gamma_r \Gamma_l}{4} \right)^2 \quad \text{and} \quad b = \frac{\Gamma_r^2}{4} + \frac{\Gamma_l^2}{4} - 2v_{sl}^2.$$

We can solve this by using the integrals,<sup>14</sup>

$$\int \frac{dx}{R_2} = \frac{c}{h} \left\{ \int \frac{dx}{cx^2 + f} - \int \frac{dx}{cx^2 + g} \right\} \quad (h^2 > 0), \quad (B2)$$

$$\int \frac{x^2 dx}{R_2} = \frac{g}{h} \int \frac{dx}{cx^2 + g} - \frac{f}{h} \int \frac{dx}{cx^2 + f} \quad (h^2 > 0), \quad (B3)$$

with

$$R_2 = a + bx^2 + cx^4, \quad h^2 = b^2 - 4ac,$$

$$f = \frac{1}{2}b - \frac{1}{2}\sqrt{h}, \quad g = \frac{1}{2}b + \frac{1}{2}\sqrt{h}.$$

Because

$$h^2 = b^2 - 4ac$$

$$\approx \frac{1}{16}(\Gamma_r^2 - \Gamma_l^2)^2 - v_{sl}^2(\Gamma_r - \Gamma_l)^2 \quad \Gamma_r \ll \Gamma_l$$

$$\approx \frac{1}{16}\Gamma_l^4 - v_{sl}^2\Gamma_l^2 \approx \Gamma_l^2 \left( \frac{1}{16}\Gamma_l^2 - v_{sl}^2 \right).$$

We can use Eqs. (B2) and (B3), if  $|v_{sl}| < |\Gamma_l/4|$ , since then  $h^2 > 0$ .

Then:

$$\begin{aligned}
\int_{-\infty}^{\infty} \frac{dx}{cx^2 + f} &= \pi \sqrt{\frac{1}{c \cdot f}}, \quad \int_{-\infty}^{\infty} \frac{dx}{cx^2 + g} = \pi \sqrt{\frac{1}{c \cdot g}}, \\
\int_{-\infty}^{\infty} \frac{dx}{R_2} &= \frac{c}{h} \left\{ \pi \sqrt{\frac{1}{cf}} - \pi \sqrt{\frac{1}{cg}} \right\} \\
&= \frac{\pi \sqrt{c}}{h} \left( \sqrt{\frac{1}{f}} - \sqrt{\frac{1}{g}} \right), \\
\int_{-\infty}^{\infty} \frac{x^2 dx}{R_2} &= \frac{g}{h} \pi \sqrt{\frac{1}{cg}} - \frac{f}{h} \pi \sqrt{\frac{1}{cf}} \\
&= \frac{\pi}{h \sqrt{c}} \{ \sqrt{g} - \sqrt{f} \}.
\end{aligned}$$

So

$$\begin{aligned}
E_s &= \frac{\Gamma_r}{2\pi} \left[ \frac{\pi}{h \sqrt{c}} (\sqrt{g} - \sqrt{f}) \right. \\
&\quad \left. + \frac{\Gamma_l^2}{4} \frac{\pi \sqrt{c}}{h} \left( \sqrt{\frac{1}{f}} - \sqrt{\frac{1}{g}} \right) \right] \\
&= \frac{\Gamma_r}{2h} \left[ (\sqrt{g} - \sqrt{f}) - \frac{\Gamma_l^2}{4} \left( \sqrt{\frac{1}{g}} - \sqrt{\frac{1}{f}} \right) \right].
\end{aligned}$$

If we restrict ourselves to the limit where

$$\Gamma_l \gg \Gamma_r, \quad \Gamma_l/4 \gg v_{sl} \quad \text{and} \quad \Gamma_l \Gamma_r \ll 4v_{sl}^2 \quad \text{we have}$$

$$\begin{aligned}
h &\approx \Gamma_l \sqrt{\frac{1}{16}\Gamma_l^2 - v_{sl}^2} \approx \frac{\Gamma_l^2}{4} \sqrt{1 - 16 \frac{v_{sl}^2}{\Gamma_l^2}} \\
&\approx \frac{\Gamma_l^2}{4} - 2v_{sl}^2 - \frac{8v_{sl}^4}{\Gamma_l^2} \\
&\approx \frac{\Gamma_l^2}{4} \left( 1 - \frac{8v_{sl}^2}{\Gamma_l^2} - \frac{32v_{sl}^4}{\Gamma_l^4} \right),
\end{aligned}$$

$$\begin{aligned}
g &= \frac{b}{2} + \frac{h}{2} \approx \frac{\Gamma_l^2}{4} - 2v_{sl}^2 - \frac{4v_{sl}^4}{\Gamma_l^2} \\
&\approx \frac{\Gamma_l^2}{4} \left( 1 - \frac{8v_{sl}^2}{\Gamma_l^2} - \frac{16v_{sl}^4}{\Gamma_l^4} \right),
\end{aligned}$$

$$f = \frac{b}{2} - \frac{h}{2} \approx \frac{4v_{sl}^4}{\Gamma_l^2}.$$

Using the expansions:

$$\sqrt{1-x} \approx 1 - \frac{1}{2}x - \frac{1}{8}x^2 \quad (\text{for } \sqrt{g}),$$

$$1/\sqrt{1-x} \approx 1 + \frac{1}{2}x + \frac{3}{8}x^2 \quad (\text{for } 1/\sqrt{g}),$$

$$1/(1-x) \approx 1 + x + x^2 \quad (\text{for } h).$$

And leaving out all terms with a power higher than  $(v_{sl}/\Gamma_l)^4$  we find

$$\begin{aligned}
E^s &= \frac{\Gamma_r}{2} \left[ \frac{\Gamma_l}{2} \left( \frac{\Gamma_l^2}{4v_{sl}^2} - 12 \frac{v_{sl}^2}{\Gamma_l^2} - 48 \frac{v_{sl}^4}{\Gamma_l^4} \right) \right. \\
&\quad \left. \times \frac{4}{\Gamma_l^2} \left( 1 + \frac{8v_{sl}^2}{\Gamma_l^2} + 96 \frac{v_{sl}^4}{\Gamma_l^4} \right) \right].
\end{aligned}$$

In our limit this can be approximated by

$$E_s \approx \frac{\Gamma_r \cdot \Gamma_l}{4v_{sl}^2}.$$

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